THE FLUORESCENCE OF THE WURSTER'S BLUE RADICAL CATION IS CONTROLLED BY A CONICAL INTERSECTION

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The photochemistry and photophysics of a stable N,N,N',N'- tetramethyl-*p*-phenylenediamine radical cation (commonly known as Wursters Blue) is the subject of current research interest as it represents an example of mixed valence (MV) compound. In this work we used *ab initio* CASSCF/CASPT2 quantum chemical calculations to map its first excited state (D_1) potential energy surface in the gas-phase.

According to the spectral data by Grilj et al., the fluorescence of Wursters Blue radical cation could only be observed at low temperatures (below 115K). In order to explain this behavior, the conical intersection space (IS) between the first excited (D_1) and the ground state (D_0) potential energy surfaces was mapped and characterized. The intrinsic reaction coordinate (IRC) scan, following the relaxation of the Wursters blue molecule from the D_1/D_0 intersection space along the D_0 potential energy surface, led to the ground state equilibrium structure. The energy barrier between the excited state energy minimum and the lowest lying conical intersection structure (CI) was calculated to be 3.1 kcal/mol. As a result, we concluded that this barrier was responsible for the observed temperature dependence of the fluorescence that disappears at temperatures above 115K due to the opening of a radiationless deactivation channel.